

CONF - 860645 - - 1

LA-UR -86-2310

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-38.

LA-UR--86-2310

DE86 013856

TITLE: EFFECTS OF MOLECULAR MOBILITY ON HIGH RESOLUTION
SOLID STATE NMR SPECTRA -- MODEL SYSTEMS

AUTHOR(S): William L. Earl

SUBMITTED TO: Proceedings ACS 8th Rocky Mountain Regional Meeting,
Denver, Colorado, June 8-12 1986.
(R. L. Wershaw and M. Mikita, Eds.)

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

 **Los Alamos** Los Alamos National Laboratory
Los Alamos, New Mexico 87545

**EFFECTS OF MOLECULAR MOBILITY ON
HIGH RESOLUTION SOLID STATE NMR SPECTRA
-MODEL SYSTEMS-**

William L. Earl

Group INC-4, Los Alamos National Laboratory

Los Alamos, New Mexico 87545

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

INTRODUCTION

Nuclear Magnetic Resonance (NMR) has long been a useful tool for physicists and chemists of all types. Until about 1970, NMR in solids was characterized by broad lines and poor sensitivity with the consequence that most studies involved the analysis of relaxation times and second moments to obtain essentially physical information¹. At that time, John Waugh's research group at MIT made several significant advances which ushered in "high resolution" NMR of solid materials. Specifically, they introduced multipulse homonuclear decoupling schemes which apply to dense spin systems *e.g.* protons in organic solids^{2,3}. These schemes will not be discussed at this symposium but relevant to this discussion, they combined a variety of cross polarization techniques due to Hartmann and Hahn⁴ and others with high power proton decoupling which had been demonstrated by Bloch⁵ and Sarles and Cotts⁶, resulting in intermediate resolution spectra of dilute spins in a bath of protons. They also suggested the application of magic angle sample spinning, a technique which had been used by Andrew⁷ and Lowe⁸ to diminish homonuclear dipole coupling, to the cross polarization-proton decoupled spectra to eliminate the chemical shift anisotropy⁹⁻¹¹. It was not until 1973 that Stejskal and Schaefer¹², Garroway¹³, and Lippmaa¹⁴ independently demonstrated the advantages of the combination of all of these techniques to the NMR of organic solids. The result is high resolution spectroscopy of a variety of spin 1/2 nuclei (primarily ¹³C, ¹⁵N, ²⁹Si, and ³¹P) in many different types of solid materials. There are a number of excellent texts and review articles to which the reader is referred for detailed information about the technique¹⁵⁻²³.

The advent of commercial spectrometers capable of routine high resolution solid state NMR has resulted in a proliferation of publications in the field. The promise has been held forth of an accurate means to obtain quantitative information about the chemical nature of carbon in a large number of heterogeneous intractable organic materials, including a variety of organic geochemicals. Unfortunately, the cross polarization technique is normally not

an equilibrium technique, consequently the intensity of the signals obtained is a function of several relaxation times, experimentally applied delays, and pulses. There have been a number of papers which have addressed the problem of quantification of cross polarization spectra from model compounds to heterogeneous mixtures^{11,24-28}.

It is the intention of this paper to point to some of the problems due to molecular motion and to suggest a few solutions to those problems. A few examples will be presented of model systems which demonstrate the effects of motion on the NMR spectroscopy and a very qualitative example of severe spectral distortion in fulvic acids will be shown. In the following discussions we will use concepts derived from the oft repeated thermodynamic picture shown in figure 1. When dealing with a homogeneous, pure compound this picture is sufficient but in a heterogeneous mixture, it is likely that there will be different compounds and different domains all with slightly different versions of figure 1 with poor thermodynamic contact between them. Thus optimal conditions for cross polarization in one domain may be totally inappropriate for another.

The following discussion will be directed towards ^{13}C NMR of organic solids, generally with high power proton decoupling, magic angle sample spinning (MAS), and cross polarization (CP). Consequently the abundant spins will be designated as I or ^1H interchangeably and the dilute spins as S or ^{13}C . There may be some very subtle differences if one were to consider the details of high resolution NMR of one of the other spin 1/2 nuclei in the solid. We will neglect quadrupolar nuclei and couplings between spin 1/2 nuclei and quadrupolar nuclei. The model interactions to be discussed are: chemical exchange, the effect of motion on high power proton decoupling, incomplete averaging of the chemical shift anisotropy, the effects of motion on the relaxation times T_{1S} and T_{1I} , and a discussion of the effects of motion on the overall cross polarization dynamics. In each case a description of the theory in physical terms will be presented, followed by a spectroscopic example. The discussion will be qualitative rather than rigorous. For complete

mathematical descriptions of the theory, the reader is referred to one of the monographs on NMR of solids, one of the review articles, or the original publications cited.

CHEMICAL EXCHANGE

Hahn and Maxwell first used NMR to measure chemical exchange processes in liquids²⁹. Since then there have been a variety of techniques used to elucidate exchange networks and determine rate constants^{30,31}. The classic experiments involve following the broadening and coalescence of two NMR peaks as temperature is increased (exchange rate is increased)³². There have been several studies of chemical exchange in solids in which the same type of behavior has been observed³³⁻³⁶. Figure 2 shows the cross polarization magic angle sample spinning (CP MAS) spectra of phthalocyanine as a function of temperature. The process being monitored is the double proton exchange shown in figure 3. In the lowest spectrum (330 K) there is an exchange narrowed peak at about 145 ppm which is the coalescence of two peaks in the upper spectrum at about 155 and 135 ppm. In the upper spectrum (180 K) the chemical exchange is frozen out by the low temperature. In order to sort out the details of this chemical exchange, it was necessary to resort to two dimensional NMR spectroscopy³⁷. The peaks noted are due to carbons a and a' in the structures of figure 3. In principal, there are similar effects for all of the carbons in this molecule but they can only be observed for carbons a and b, the shifts between c and c' and d and d' are not even resolved in the 2-D spectrum.

As far as the quantification of CP MAS spectra is concerned, the interesting spectrum is the middle one of the series (240 K). In this spectrum, the intensity due to carbon a is virtually lost by virtue of exchange broadening. Similar proton exchanges or even more complicated exchange processes may be present in any given sample and consequently spectral intensity in any dynamic system may be lost through exchange broadening.

As an aside, we would like to point out that the spectra in the non exchanging (180 K) and exchange narrowed (330 K) spectra must be fit with a Gaussian line shape because they are undoubtedly due to a dispersion of chemical shifts. (The line width in the majority of solid state NMR spectra is determined by a dispersion in chemical shifts, not by T_2 , therefore the line shape is not cleanly defined but is much closer to a Gaussian than a Lorentzian.) The exchange broadened spectra, on the other hand are Lorentzian because the line shape is determined by the exchange. It is also worth mentioning that there are subtle interactions between the chemical exchange and the spinning when the spinning speed and exchange rate are equal³⁸. These interactions may produce very distorted spectra. We have calculated such spectra for chemically exchanging systems in very limited cases and it is clear that simple McConnell exchange theory is inappropriate. However the errors in estimated rate constants are probably no greater than 10% except in unusual cases.

PROTON DECOUPLING

Molecular motion can defeat the effects of proton decoupling, resulting in extremely broad lines. Qualitatively, this effect can be understood as follows: In the absence of proton decoupling, each carbon is dipole-dipole coupled to every proximate proton. That coupling produces a shift in the carbon resonance, dependent upon the distance and the angle between the C-H internuclear vector and B_0 . In most organic solids, the proton density is great enough that there is strong coupling between the individual protons and mutual spin flips (spin exchange)¹. The result of this physical situation is a broad carbon resonance. The application of high power proton decoupling is a coherent averaging phenomenon which essentially reduces the C-H dipole interaction^{5,6}. Effectively, the proton moments are rotated coherently about the decoupling field, B_1 . If, during that rotation there is

a molecular motion which changes the orientation of the C-H vector it will act to undo the averaging effect³⁹. In the context of relaxation theories, when motion has an inverse correlation time equal to the interaction the relaxation is most effective. In the case of proton decoupling, molecular motion with an inverse correlation time equal to the decoupling field strength (expressed in frequency units) will have maximal effect increasing the linewidth *i.e.* if $1/\tau_c = \gamma B_1$. Linewidth contributions from molecular motion have been discussed in the literature and equations presented for the relaxation expected in terms of the C-H second moment and the spectral density of motion^{17,40,41}. The authors point out that for "normal" experimental conditions, isotropic motion with a correlation time of 70 μ s results in a linewidth of 3.7 kHz⁴¹. This is clearly capable of causing a high resolution peak to "disappear" into the baseline. Usually, motion in solids is not isotropic and consequently line widths of this predicted magnitude are not usually seen but effects an order of magnitude smaller are sufficient to cause problems. Figure 4 neatly demonstrates the effects of motion on decoupling in polyethylene oxide (PEO). The upper spectrum is a cross polarization spectrum with MAS at room temperature and the central spectrum was taken under the same conditions except without MAS. Both of these spectra are rather broad, the line shape of the MAS spectrum is neither Lorentzian nor Gaussian and the shape of the non-spinning line is not the well resolved pattern characteristic of a chemical shift tensor. The lower trace was taken under the same conditions as figure 4 A except that the temperature was lowered to $\approx -45^\circ$ C. At low temperature, the motion has been slowed to frequencies lower than 70 kHz or so and decoupling is now more effective, resulting in a slightly narrower spectral line but with a much clearer defined Gaussian line shape due to a dispersion of chemical shifts in the sample. In addition, the cross polarization is much more efficient, resulting in much better signal to noise. (This will be discussed in detail below.)

In contrast to the above, very rapid motion can reduce the C-H dipole coupling

resulting in a self decoupling. This will have the effect of giving relatively narrow ^{13}C lines with no decoupling field. This effect may be noted in figure 5 which is the CP MAS spectra of adamantane with and without high power proton decoupling. As is well known, adamantane is a relatively spherical molecule which tumbles rapidly and isotropically in the lattice site^{42,43}. The result of this motion is that the carbons are decoupled from the intramolecular protons and the remaining broadening in the coupled spectrum is due to intermolecular C-H interactions which are relatively weak because of the separation and the r^{-3} dependence. The full width at half maximum of 100 Hz seen in the proton coupled spectrum in figure 5 is acceptably narrow when compared to most ^{13}C spectra in solids, it only looks broad when compared to the abnormally narrow spectrum for decoupled adamantane. Another well known example of self decoupling may be seen in the so called dipolar dephasing experiments⁴⁴ where methyl ($-\text{CH}_3$) groups behave in a fashion similar to quaternary carbons⁴⁵. In this experiment, one relies on the linewidth in the presence of C-H coupling to destroy transverse magnetization. Since methyl groups usually exhibit propeller rotation, the C-H dipole interaction is severely attenuated and methyl transverse magnetization remains even after relatively long interruptions of decoupling.

CHEMICAL SHIFT ANISOTROPY

Molecular motion may affect MAS spectra through interactions with the chemical shift anisotropy. Conceptually, this is similar to motional line broadening interactions with the proton decoupling⁴⁶. Qualitatively, magic angle sample spinning is a coherent means of averaging the chemical shift tensor to its isotropic value and incoherent molecular motions serve to destroy that averaging. First, we must recall that MAS does not produce an isotropic system but only causes the magnetization to refocus at the end of each rotor period, eliminating the anisotropy in the chemical shift. Magic angle sample spinning is

much like a Carr-Purcell⁴⁷ echo train in that there is a real refocussing of the magnetization and it is possible to Fourier transform the echoes resulting in a high resolution spectrum. In the Carr-Purcell sequence, the chemical shift is refocussed but under MAS, it is the anisotropy in the shift that gets refocussed. This concept is expressed very schematically in figure 6. If, during the rotor period, a molecule changes its orientation the chemical shift of the affected carbon will change from one instantaneous value to a different value, i.e. the spin will join a different isochromat. Consequently, that particular spin will no longer refocus, the echo amplitude illustrated in figure 6 C will be diminished, resulting in a shorter "spun free induction decay" which when Fourier transformed will give a broader ¹³C resonance. In a similar fashion to the effect of motion on decoupling, the loss of refocussing is most pronounced when the frequency of motion ($1/\tau_c$) is equal to the spinner frequency. This effect is rather subtle and has only been effectively demonstrated in a few publications^{46,48}. This type of motional line broadening will be most pronounced when the shift anisotropy is large and the motions cause large jumps within that anisotropy.

There is a very similar phenomenon; studied by Veeman and coworkers which can be demonstrated in two dimensional exchange spectra. They used a specialized version of the chemical exchange 2-D experiment in which the mixing time is equal to an integral number of rotor periods⁴⁹. In the absence of motion there are no cross peaks between spinning sidebands and the centerband. Such cross peaks appear only when there is motion at the spinner frequency. This experiment can be exploited to obtain information about the spectral density of motion at very low frequencies but it would have no significant effect upon a "normal" CP or Bloch decay spectrum.

Although these are very interesting effects of molecular motion, they have only slight broadening effects and would probably be mostly unnoticed in ¹³C spectroscopy of organic geochemicals. However, these effects may be exploited if the researcher begins to ask more complicated questions about the details of molecular dynamics in complex heterogeneous

systems.

CROSS RELAXATION TIMES (T_{1S})

There are a number of publications in the literature which deal with cross polarization spin dynamics. Waugh and coworkers concerned themselves with the detailed theory for static systems^{10,25} and later Cheung and Yaris²⁶ extended the theory to dynamic systems. In order to obtain accurate information about C-H couplings or detailed motional parameters, it is necessary to delve into the details of the theory. Since this discussion is primarily concerned with motional effects on spectroscopic parameters, it is sufficient to refer to figure 1 and note that there is a rate constant, $1/T_{1S}$ which describes the rate of transfer of magnetization from the proton bath to the carbon spins. That rate constant is proportional to the strength of the C-H coupling. Although magnetization can be transferred via the indirect (J) coupling⁵⁰, most solid state CP spectroscopy relies on the dipole-dipole interaction. In the simplest analysis, the C-H dipole interaction is attenuated by molecular motion. Consequently the value of T_{1S} increases with molecular motion and with isotropy of that motion. There are several limiting cases which are worth discussing in some detail. First, in the limit of no motion, T_{1S} is dependent upon the number and proximity of protons so a methyl carbon would be expected to have a much shorter cross relaxation time than a methine carbon. Intermolecular cross polarization is attenuated by the distance, but can provide a significant contribution simply because of the large number of neighbors possible and in specific cases intermolecular C-H distance may be very short, *eg.* in stacked benzene ring systems. If the motion is very fast but anisotropic, the dipole interaction will be attenuated but may still be quite significant depending on the details of the averaging of the dipole tensors. In the case of rapid, isotropic motion, the intramolecular C-H dipole coupling will vanish but intermolecular coupling may be strong enough have

a value of T_{1S} short enough for cross polarization. The prime example of this behavior is adamantane at room temperature. Although there is no intramolecular cross polarization, the intermolecular C-H interaction is strong enough to result in a T_{1S} of about 1 s for usual experimental conditions which makes cross polarization difficult but possible⁴³. Finally, in the limit of isotropic rotation with translational motion, the C-H dipole interaction will vanish over the time scale of tens of μ s and there will be no cross polarization through the dipole interaction. In this limit, although the sample may appear to be solid to a casual observer, to the NMR spectroscopist it is a "liquid". In exceptional cases (an extremely stable spectrometer, very accurate adjustment of the Hartmann-Hahn matching condition, and long contact times) carbon magnetization may be obtained through the J cross polarization mechanism even under conditions of rapid motion because the J coupling tensor has a non-zero average with motion. To date, this type of magnetization transfer has not been documented in solids although it is quite useful in liquid state NMR spectroscopy.

In summary, molecular motion will usually lengthen the value of T_{1S} relative to static systems and this can be accommodated in a normal cross polarization experiment through lengthening the contact time. Trade offs of this solution and greater details of cross polarization dynamics are presented below.

ROTATING FRAME RELAXATION ($T_{1\rho}$)

The "standard" spin lock cross polarization experiment with matched rf field strengths involves both proton and carbon rotating frame magnetization. First, spin locked proton magnetization is generated, quantized along the proton rf field. In spin thermodynamic terms this is an ordered system which is equivalent to cooling the proton spin bath⁵¹. Then the cross polarization contact is made during which time the carbon bath is cooled, hopefully to match the proton spin temperature. This has the effect of creating carbon

magnetization, spin locked along the ^{13}C rf field. During any spin lock, the magnetization is formally quantized along the rf field and will decay with a characteristic time constant, $T_{1\rho}$ or the rotating frame T_1 . This relaxation can be thought of as warming the spin locked spin bath. In general, the $T_{1\rho}$ of both the I and S spins contribute to the loss of magnetization during the cross polarization contact but usually $T_{1\rho}(^{13}\text{C})$ is much longer than $T_{1\rho}(^1\text{H})$ so it is only proton relaxation that is usually considered. There are exceptions to this rule, in cases where the ^{13}C line width is very broad and dominated by motion, it is possible that the carbon relaxation is the primary contributor^{52,53}. For a complete discussion of cross polarization dynamics, the reader is referred to one of the excellent publications on the subject.

Since $T_{1\rho}(^1\text{H})$ is a relaxation time, it will be affected by molecular motion and as mentioned several times above, motion at the frequency of the interaction will have maximal efficiency in shortening $T_{1\rho}$. The motional frequency of interest is the intensity of the spin locking rf field expressed in frequency units, γB_1 ⁵⁴. Note that this is the spin locking field during the cross polarization contact. In some cases the experimenter may change the B_1 strength after cross polarization, using a different intensity for proton decoupling. For the majority of cross polarization experiments this is between 30 and 80 kHz or relatively low frequency motion. In most solids molecular motions will serve to shorten the proton $T_{1\rho}$. This will have the effect of reducing cross polarization efficiency or entirely eliminating cross polarization. Since $T_{1\rho}$'s may be much less than a millisecond, during a normal contact of 1-5 ms the proton bath will warm up and begin to warm the ^{13}C bath which will destroy ^{13}C magnetization created at the very beginning of the contact. Referring to figure 1 and the timing of a spin lock cross polarization experiment, at the start of CP the proton reservoir is cold, the CP contact is made and heat flows from the carbons to the protons. After some time of the order of $T_{1\rho}(^1\text{H})$, the proton bath will have warmed up due to this relaxation and heat will begin to flow back into the carbons at a

rate determined by $1/T_{1S}$. After times much greater than $T_{1\rho}(^1\text{H})$ both the carbon and the proton systems will reach lattice temperature and all magnetization will be destroyed.

In the limit of very fast motion, $T_{1\rho}(^1\text{H})$ may get quite long, *i.e.* extreme narrowing. This is the case with adamantane, where although T_{1S} has been lengthened by motion, the $T_{1\rho}$'s are so long that some cross polarization can be obtained with long contact times (>10 ms). The signal intensity versus relaxation times will be discussed in the following section on overall spin dynamics.

It should also be mentioned that although $T_{1\rho}$ is written as a spin lattice relaxation time, if the γB_1 is not very large there can be motional contributions which produce strong spin-spin character in $T_{1\rho}$. This is especially significant in complex samples where there may be paramagnets which may act as a sink for magnetization and proton-proton flip flops will act as a mechanism of transporting magnetization to the paramagnets resulting in a very short $T_{1\rho}(^1\text{H})$.

Figure 7 demonstrates an interesting and significant expression of the effects of rotating frame relaxation on a ^{13}C cross polarization spectrum. The spectra are of polyethylene oxide which is a primarily noncrystalline polymer with a spectrum of motional frequencies in the tens to hundreds of kHz range⁵⁶. The upper trace (A) is the spectrum obtained with matched 35 kHz ^1H and ^{13}C rf fields and the lower trace was obtained under identical conditions except that the rf fields were increased to 76 kHz. There were 4 times the number of scans taken for the upper spectrum but other than that they are normalized to equal intensities *i.e.* there is more than four times the intensity in the lower spectrum. At room temperature, the relaxation is near the $T_{1\rho}$ minimum. By increasing γB_1 , $T_{1\rho}$ is increased and cross polarization is more effective. There is also a discrimination favoring rapid motions at the higher γB_1 and signal has been gained from portions of the sample with relatively short T_2 's (amorphous regions) resulting in a very broad base in the lower

spectrum. The rather odd line shapes seen in this figure and in figure 4 are the result of a distribution of chemical shifts, incomplete proton decoupling, and a distribution of motional frequencies. This example suggests that one way to alleviate problems due to short $T_{1\rho}$'s is to use very high rf fields.

OVERALL SPIN DYNAMICS

In the final analysis, what are the overall effects of molecular motion on the spin dynamics which are critical to generating signal in spin lock cross polarization experiments? Figure 8 shows three plots of signal intensity versus cross polarization contact time for three different combinations of cross relaxation time T_{IS} and proton $T_{1\rho}$. The dotted line is the case of very long $T_{1\rho}$ and short T_{IS} . Under these conditions, the carbon signal intensity is generated quickly, before the proton spins "warm up". The carbon intensity will be maximal and the value selected for the contact time is not critical to obtaining quantitative ^{13}C intensity. The solid line represents the more usual case where the two relaxation times are similar enough that if the contact time is selected carefully, quantitative intensity may be obtained but there is a relatively narrow window of contact times which will be quantitative. The dashed line represents the final extreme, where the $T_{1\rho}(^1\text{H})$ is relatively short compared to the T_{IS} and it is not possible to get complete cross polarization before the magnetization decays back into the rapidly relaxing proton system.

In a pure solid with no phase separations, the ^{13}C signal intensity will follow a curve much like one of the above. One expects that the proton $T_{1\rho}$ will be constant throughout the sample and that T_{IS} may vary from carbon to carbon due to proximity to protons *ie.* quarternary carbons may have longer T_{IS} 's than methylene carbons. Molecular motion will weaken the C-H dipolar coupling which is the mechanism for cross relaxation and it will cause $T_{1\rho}(^1\text{H})$ to shorten resulting in a curve which approaches the dashed line in

figure 8. If the system were homogeneous, this would be a problem only in that the signal to noise would be attenuated by the incomplete cross polarization. Unfortunately, in most natural products homogeneity is the exception rather than the rule and one usually finds small domains with differing mobilities. There is generally poor thermal contact between the protons in different domains resulting in different $T_{1\rho}(^1\text{H})$'s for the different regions. In addition there will be differences in T_{1s} from carbon to carbon in a single domain as well as differences due to varying mobility between domains. The result is that there may be excellent cross polarization in one domain while it is weak or nonexistent in another. A nice example of this effect can be seen in corn seeds where the starch is fairly rigid and cross polarizes nicely while the corn oils are mobile and probably in small pockets and will not cross polarize at all⁵⁶. Figure 9 is two room temperature spectra of intact corn seeds. The upper spectrum is the Fourier transform of a Bloch decay with MAS and high power proton decoupling. (A Bloch decay is the free induction signal resulting after a $\pi/2$ pulse or some other flip angle which generates xy magnetization in the spins to be observed⁵⁷.) The delay time between pulses was too short for adequate ^{13}C longitudinal relaxation in the rigid starch so the carbohydrate signals are somewhat attenuated⁵⁸. However, the sharp aliphatic peaks for the oils stand out quite nicely. The lower spectrum is the same sample but the magnetization was generated via cross polarization. In this case the signals due to the oils are virtually absent. In the context of figure 8, the starch molecules correspond to a system which follows a curve much like number 1 and the oils are more extreme than curve number 3.

A FULVIC ACID EXAMPLE

There is a belief among many researchers that many of the details discussed above are simply curiosities and do not apply in "real" systems. We have performed a cursory

investigation of several fulvic acids which indicates that motional effects may dominate the spectra⁵⁹. The rationale for this study was an inability to obtain solid and solution NMR spectra of fulvic acids which agreed in overall spectral shape. The solution spectra were acquired with long delays between pulses and it was believed that they were correct which called into question the accuracy of the cross polarization spectra. The sample discussed here is an Armadale fulvic acid which was lyophilized and appeared quite dry. Figure 10 contains three spectra of the sample taken under different experimental conditions. The bottom spectrum (C) is a cross polarization spectrum taken at room temperature. The central spectrum is the Fourier transform of a Bloch decay taken with a recycle time of 3.0 s. It is probable that this recycle time is too short to get full T_1 relaxation so the spectrum is probably distorted but it serves to demonstrate that there is significant intensity missing in the low field portion of spectrum C. The upper spectrum (A) is a cross polarization spectrum taken under virtually identical conditions as spectrum C except that the temperature was lowered to $\approx -55^\circ$ C. There are two significant observations to be made. First, the relative intensities in different portions of the spectrum nearly match those obtained in careful solution NMR experiments. Second, the signal to noise in the aliphatic region of the spectrum is approximately 4 times better than in the same spectral region of the cross polarization spectrum at room temperature. The reason for both of these differences is that molecular motion at room temperature has both shortened $T_{1\rho}$ and lengthened T_{1S} so the magnetization is following a curve much like curve 3 in figure 8. By cooling the sample the motion has apparently been frozen out resulting in both longer $T_{1\rho}$'s and shorter T_{1S} 's so the magnetization is following a curve between curves 1 and 2. The signal to noise improvement results from efficient cross polarization with a cross polarization enhancement of close to the factor of four expected. We have not investigated the details of the molecular motion in this sample, nor have we performed a variable temperature study to determine whether all significant motion ceases at the same temperature or whether there are a series of different activation energies for molecular

motion in this sample. The intention of this experiment was simply to get a spectrum in which the relative carbon intensities truly reflected the concentration of the carbon species in the sample for accurate quantitative analysis.

EXPERIMENTAL DIRECTIONS

There are several experimental solutions to many of the problems in cross polarization ^{13}C NMR which have been suggested in the discussion above. Very high γB_1 's for both cross polarization contacts and proton decoupling will aid in lengthening $T_{1\rho}$'s as well as ameliorating the problems of line broadening due to inability to adequately decouple protons. It is relatively easy to obtain very high powered rf amplifiers and generate the needed rf levels but it is more difficult to build probes capable of handling these rf levels. In any case, if heating and probe arcing can be controlled, larger B_1 fields are almost always an advantage. A second possible solution to motional problems is to resort to Bloch decays as a method of generating magnetization. This suffers due to a loss of the theoretical enhancement of four from cross polarization but as seen above, that gain may not be realized when molecular motion makes a large contribution to the spectrum. A more significant problem is the fact that the carbon T_1 's may vary through the sample and in order to get a quantitatively accurate spectrum it is necessary to wait several T_1 's which in a solid could be hundreds of seconds. Another solution is to take a series of spectra of the same sample as a function of cross polarization contact time and generate curves equivalent to those in figure 8 which can be computer fit with the equilibrium intensity as one of the parameters. This is a tedious process requiring at least 10 points per curve to determine $T_{1\rho}$, T_{1s} , and intensity. It also suffers because there are clearly samples for which no cross polarization can be obtained such as the oil in the corn seeds above. Finally, the most practical solution to motional problems is to stop the motion through

variable temperature CP spectroscopy. At present it is possible to purchase nominally variable temperature probes from several manufacturers which will conveniently reach temperatures around -80° C. There are two significant experimental difficulties. First, the probe tuning varies seriously with temperature and must be carefully rematched when the temperature is changed and the temperature must be relatively stable over the time of the cross polarization experiment. Secondly, proton T_1 's usually lengthen with decreasing temperature so one must be cautious to use a repetition time commensurate with the relaxation time. For this it will be necessary to perform variable temperature studies of "generic" samples to get a qualitative idea of the optimal temperature and recycle time.

Finally, the "problem" of quantification of solid state NMR spectra is no longer a serious problem. The technique is mature enough and the magnetic phenomena are well enough understood that with some care it should be possible to be good data on most samples. The challenge is now to use the "complications" to the experimenter's advantage to obtain more information. For example determining the frequencies and amplitudes of motion for different domains of humic materials and including that information in the structural model to get a truly self consistent picture of the overall structure.

ACKNOWLEDGEMENTS

The author would like to thank Robert Wershaw and Kevin Thorn for collaboration and discussions on the problem of molecular mobility in fulvic acids. Very special thanks are due to Beat Meier who performed the experimental work on pñthalocyanine and who has contributed through many interesting discussions. This work was performed under the auspices of the U.S. Department of Energy.

REFERENCES

1. A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, Oxford (1961).
2. J.S. Waugh, L.M. Huber, and U. Haeberlen, *Phys. Rev. Lett.* **20**, 180 (1968).
3. U. Haeberlen, High Resolution NMR in Solids, Academic Press, New York (1976) Supplement 1 to Advances in Magnetic Resonance, J.S. Waugh (ed).
4. S.R. Hartmann and E.L. Hahn, *Phys. Rev.* **128**, 2042 (1962).
5. F. Bloch, *Phys. Rev.* **111**, 841, (1958).
6. L.R. Sarles and R.M. Cotts, *Phys. Rev.* **111**, 853 (1958).
7. E.R. Andrew, *Arch. Sci. (Geneva)* **12**, 103 (1959).
8. I.J. Lowe, *Phys. Rev. Lett.* **2**, 285 (1959).
9. A. Pines, M.G. Gibby, and J.S. Waugh, *Bull. Am. Phys. Soc.* **16**, 1403 (1971).
10. A. Pines, M.G. Gibby, and J.S. Waugh, *J. Chem. Phys.* **56**, 1776 (1972).
11. A. Pines, M.G. Gibby, and J.S. Waugh, *J. Chem. Phys.* **59**, 569 (1973).
12. J. Shaefer, E.O. Stejskal, and R. Buchdahl, *Macromolecules* **8**, 291 (1975).
13. A.N. Garroway, W.B. Moniz, and H.A. Resing, *Preprints of the Div of Organic Coatings and Plastics Chem.* **36**, 113 (1976).
14. E. Lippmaa, M. Alla, and T. Tuherm, *Proc. XIX Congress Ampere, Heidelberg* 113 (1976).
15. C.A. Fyfe, Solid State NMR for Chemists, C.F.C Press, Guelph (1983).
16. D.E. Axelson, Solid State Nuclear Magnetic Resonance of Fossil Fuels, Multiscience Publications, Montreal (1985).
17. M. Mehring, Principles of High Resolution NMR in Solids, Second Edition, Springer-Verlag, Berlin (1983).
18. C.P. Slichter, Principles of Magnetic Resonance, Second Edition, Springer-Verlag, Berlin (1980).

19. C.S. Yannoni, *Acc. Chem. Res.* **15**, 201 (1982).
20. J. R. Lyerla, C.S. Yannoni, and C.A. Fyfe, *Acc. Chem. Res.* **15**, 208 (1982).
21. J.R. Havens and J.L. Koenig *Applied Spectroscopy* **37**, 226 (1983).
22. J. Schaefer and E.O. Stejskal in Topics in Carbon-13 NMR Spectroscopy, Vol 3, G.C. Levy (ed) Wiley, New York (1979).
23. F.P. Miknis, V.J. Bartuska, and G.E. Maciel, *American Laboratory*, pp 19 ff., November (1979).
24. D.L. Vanderhant and H.L. Retcofsky, in *Preprints of the 1976 Coal Chemistry Workshop*; H.M. Peters and D.S. Ross (eds) Stanford Research Institute, Menlo Park, Calif. 202 (1976).
25. D. Demco, J. Tegenfeldt, and J.S. Waugh, *Phys. Rev. B* **11**, 4133 (1975).
26. T.T.P. Cheung and R. Yaris, *J. Chem. Phys.* **72**, 3604 (1980).
27. M.H. Levitt, D. Suter, and R.R. Ernst, *J. Chem. Phys.* **84**, 4243 (1986).
28. L.B. Alemany, D.M. Grant, R.J. Pugmire, T.D. Alger, and K.W. Zilm, *J. Am. Chem. Soc.* **105**, 2113 (1983)
L.B. Alemany, D.M. Grant, R.J. Pugmire, T.D. Alger, and K.W. Zilm, *J. Am. Chem. Soc.* **105**, 2142 (1983).
29. E.L. Hahn and D.E. Maxwell, *Phys. Rev.* **88**, 1070 (1952).
30. L.M. Jackman and F.A. Cotton, Dynamic NMR Spectroscopy, Academic Press, New York (1975).
31. A. Steigel in NMR, Basic Principles and Progress, Vol 15, P. Diehl, E. Fluck and R. Kosfeld (eds), Springer-Verlag, Berlin (1978)
H.W. Spiess in NMR, Basic Principles and Progress, Vol 15, P. Diehl, E. Fluck and R. Kosfeld (eds), Springer-Verlag, Berlin (1978).
32. H.M. McConnell, *J. Chem. Phys.* **28**, 430 (1958).
33. R.D. Miller and C.S. Yannoni, *J. Am. Chem. Soc.* **102**, 7396 (1980)
V. Macho, R.D. Miller, and C.S. Yannoni, *J. Am. Chem. Soc.* **105**, 3735 (1983)
34. P.C. Myhre, J.D. Kruger, B.L. Hammond, S.M. Lok, C.S. Yannoni, V. Macho, H.H. Limbach, and H.M. Veith, *J. Am. Chem. Soc.* **106**, 6079 (1984).

35. N.M. Szeverinyi, A. Bax, and G.E. Maciel, *J. Am. Chem. Soc.* **105**, 2579 (1983).
36. H. Dorn, B.E. Hanson, and E. Motell, *Inorg. Chim. Acta* **54**, L71 (1981).
37. B.H. Meier, C.B. Storm, and W.L. Earl, Submitted to *J. Am. Chem. Soc.*
38. B.H. Meier, Unpublished Calculations.
39. A.N. Garroway, W.B. Moniz, and H.A. Resing, A.C.S. Symposium Series 103 Chapter 4, (1979).
40. A.N. Garroway, D.L. VanderHart, and W.L. Earl, *Philos. Trans. R. London A* **299**, 609 (1981).
41. D.L. VanderHart, W.L. Earl, and A.N. Garroway, *J. Magn. Reson.* **44**, 361 (1981).
42. H. ^A. Resing, *Mol. Cryst. Liq. Cryst.* **9**, 101 (1969).
43. A. Pines and T.W. Shattuck, *J. Chem. Phys.* **61**, 1255 (1974).
44. S.J. Opella and M.H. Frey, *J. Am. Chem. Soc.* **101**, 5854 (1979).
45. L.B. Alemany, D.M. Grant, T.D. Alger, and R.J. Pugmire, *J. Am. Chem. Soc.* **105**, 6697 (1983).
46. D. Suwelack, W. Rothwell, and J.S. Waugh, *J. Chem. Phys.* **73**, 2559 (1980).
47. H.Y. Carr and E.M. Purcell, *Phys. Rev* **94**, 630 (1954).
48. B.C. Gerstein, *Carbon* **22**, 409 (1984).
49. A.F. DeJong, A.P.M. Kentgens, and W.S. Veeman, *Chem. Phys. Lett.* **109**, 337 (1984).
50. G.C. Chingas, A.N. Garroway, R.D. Bertrand, and W.B. Moniz, *J. Chem. Phys.* **74**, 127 (1981).
51. M. Goldman, Spin Temperature and Magnetic Resonance on Solids, Clarendon Press, Oxford (1970).
52. J. Schaefer, E.O. Stejskal, and R. Buchdahl, *Macromolecules* **10**, 384 (1977).
53. D.L. VanderHart and A.N. Garroway, *J. Chem. Phys.* **71**, 2773 (1979).
54. D.C. Ailion in Advances in Magnetic Resonance, Vol. 5, J.S. Waugh (ed), Academic Press, New York (1971).

55. T.M. Connor and A. Hartland, *J. Polymer Sci. A-2* **7**, 1005 (1969).
56. J. Schaefer and E.O. Stejskal, *J. Am. Oil Chem. Soc.* **51**, 562 (1974).
57. F. Bloch, *Phys. Rev* **70**, 460 (1946).
58. T.C. Farrar and E.D. Becker, Pulse and Fourier Transform NMR, Academic Press, New York (1971).
59. W.L. Earl, R.L. Wershaw, and K.A. Thorn, Manuscript in Preparation.

FIGURE CAPTIONS

FIGURE 1: A thermodynamic picture of cross polarization spin dynamics. The carbon and proton spin reservoirs may relax to the lattice temperature with time constants T_1 and $T_{1\rho}$. The cross polarization contact is established by opening the valve pictured and proceeds with the time constant T_{IS} .

FIGURE 2: A series of ^{13}C magic angle sample spinning spectra of phthalocyanine taken as a function of temperature to demonstrate the chemical exchange pictured in figure 3.

FIGURE 3: The double proton jump in phthalocyanine.

FIGURE 4: Three cross polarization magic angle sample spinning spectra of polyethylene oxide. The upper spectrum (A) was taken with magic angle sample spinning at room temperature. The middle spectrum (B) was taken with no spinning at room temperature and the bottom spectrum (C) was taken with MAS at $\approx -45^\circ \text{C}$.

FIGURE 5: Two cross polarization spectra of adamantane taken with and without high power proton decoupling.

FIGURE 6: The time development of chemical shifts and magnetization with magic angle sample spinning. The left portion of the figure demonstrates how the chemical shift of a single spin would develop with MAS. The right portion demonstrates how under static

conditions, destructive interferences due to differences in chemical shift causes the total magnetization to decay rapidly. Under the action of MAS, the chemical shifts all return to their original value at the end of each rotor period resulting in a refocussing.

FIGURE 7: Cross polarization spectra of polyethylene oxide taken with magic angle sample spinning. The top spectrum (A) was taken with 33 kHz matched ^1H and ^{13}C rf fields (γB_1) for the cross polarization contact followed by proton decoupling with the same field strength. The lower spectrum (B) was taken of the same sample under identical conditions except that the rf fields were increased to 68 kHz.

FIGURE 8: The ^{13}C signal intensity as a function of cross polarization contact time for three different idealized combinations of $T_{1\rho}(^1\text{H})$ and T_{1S} . The dotted curve (1) represents the case of very short T_{1S} and long $T_{1\rho}$. The solid curve (2) represents the case of $T_{1\rho}$ somewhat longer than T_{1S} and the dashed curve (3) the case where $T_{1\rho}$ is about equal to or somewhat shorter than T_{1S} .

FIGURE 9: Two spectra of intact corn seeds. The upper spectrum (A) is the Fourier transformation of a Bloch decay and shows several very sharp peaks due to oils in the sample. The lower spectrum (B) is the result of cross polarization and demonstrates that the mobility of the oils prevents them from cross polarizing.

FIGURE 10: Three ^{13}C spectra of Armadale fulvic acid taken under different spectroscopic conditions. The upper spectrum (A) is the cross polarization spectrum taken with a 0.5 s cross polarization contact time with the sample temperature about -56°C . The middle spectrum (B) is the Fourier transform of a Bloch decay taken with a three second repetition time between pulses. The bottom spectrum (C) is a cross polarization spectrum taken under the same conditions as spectrum A except that the temperature was approximately 20°C .

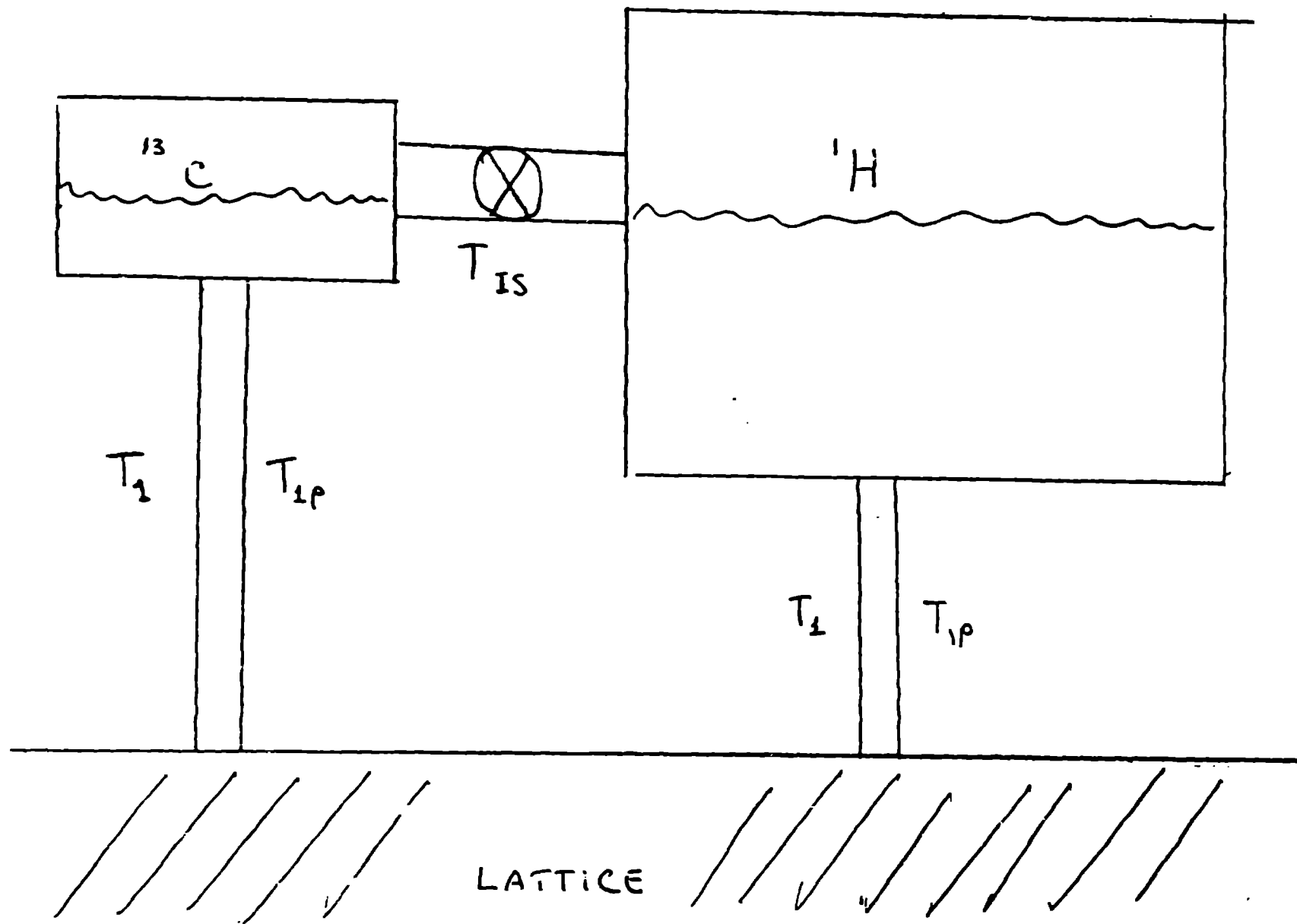


FIGURE 1

THE FINAL FIGURE
WILL CONTAIN ONLY
THESE SPECTRA

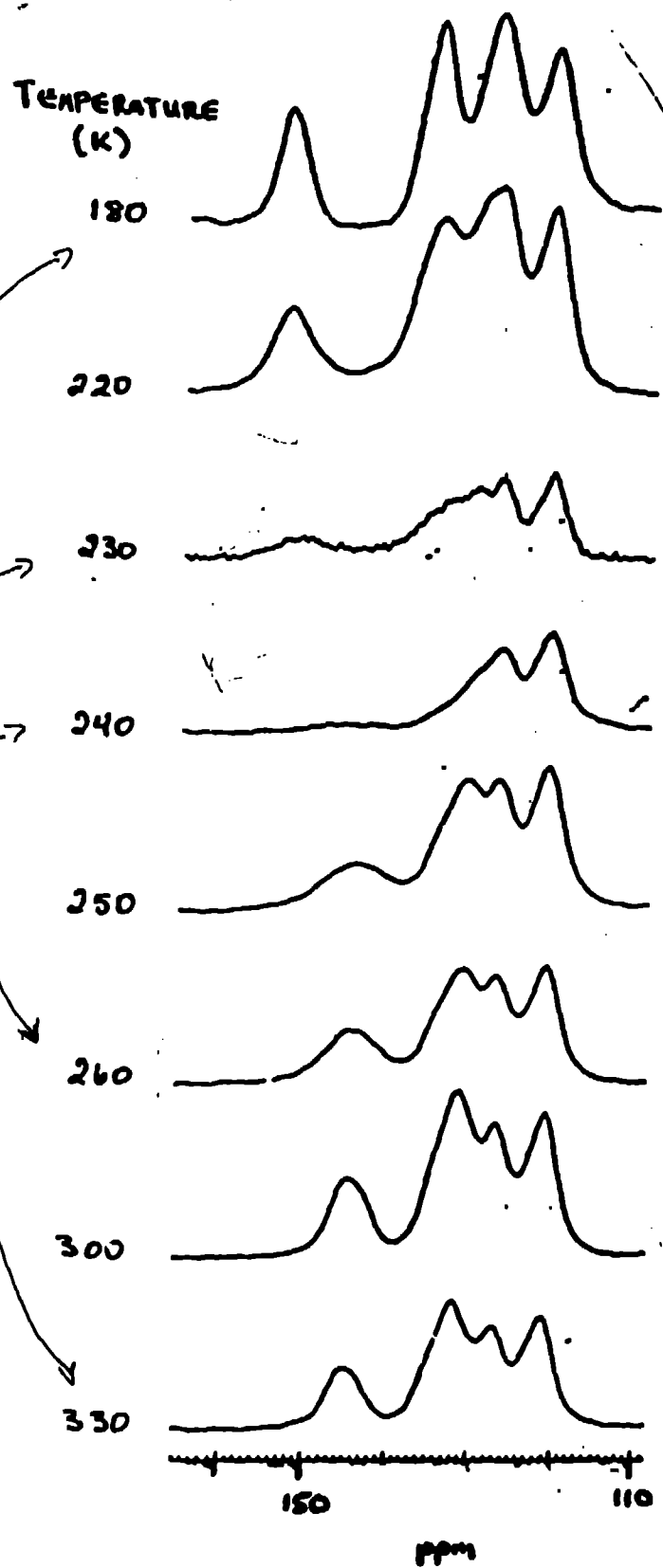


FIGURE 2

PHTHALOCYANINE

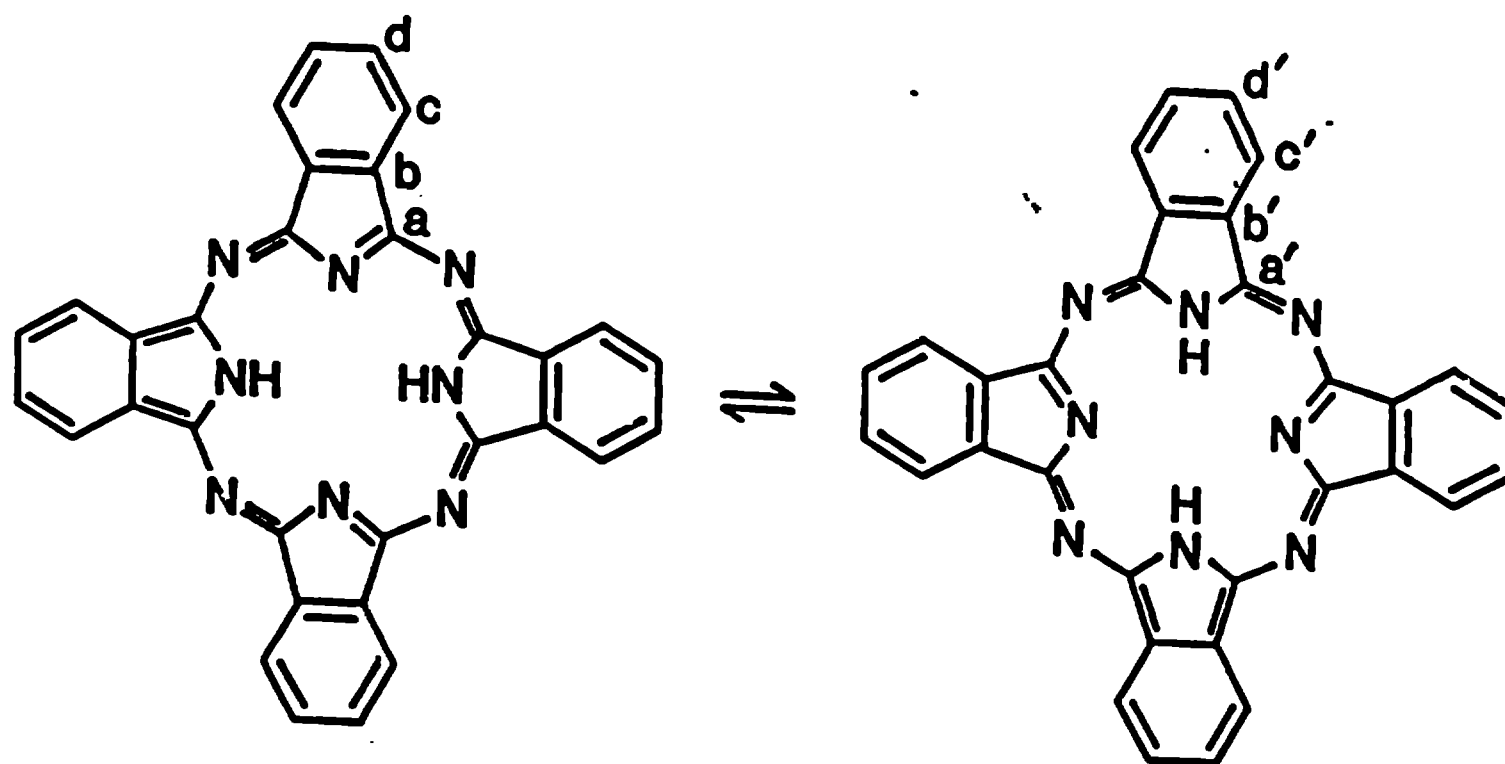


Figure 3.

FIGURE 4

POLYETHYLENE
OXIDE

MAS
20°C

A

STANC
20°C

B

MAS
-45°C

C

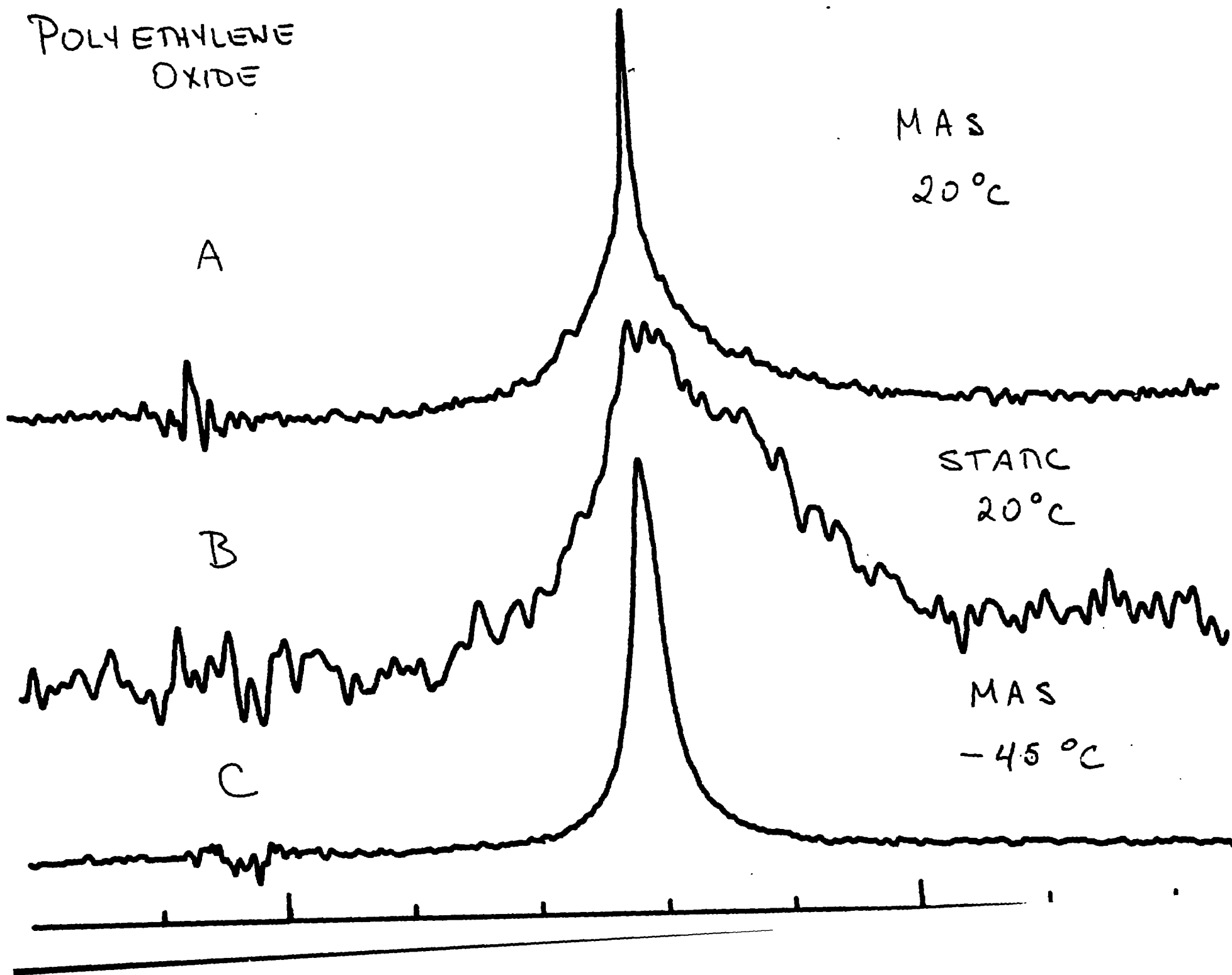
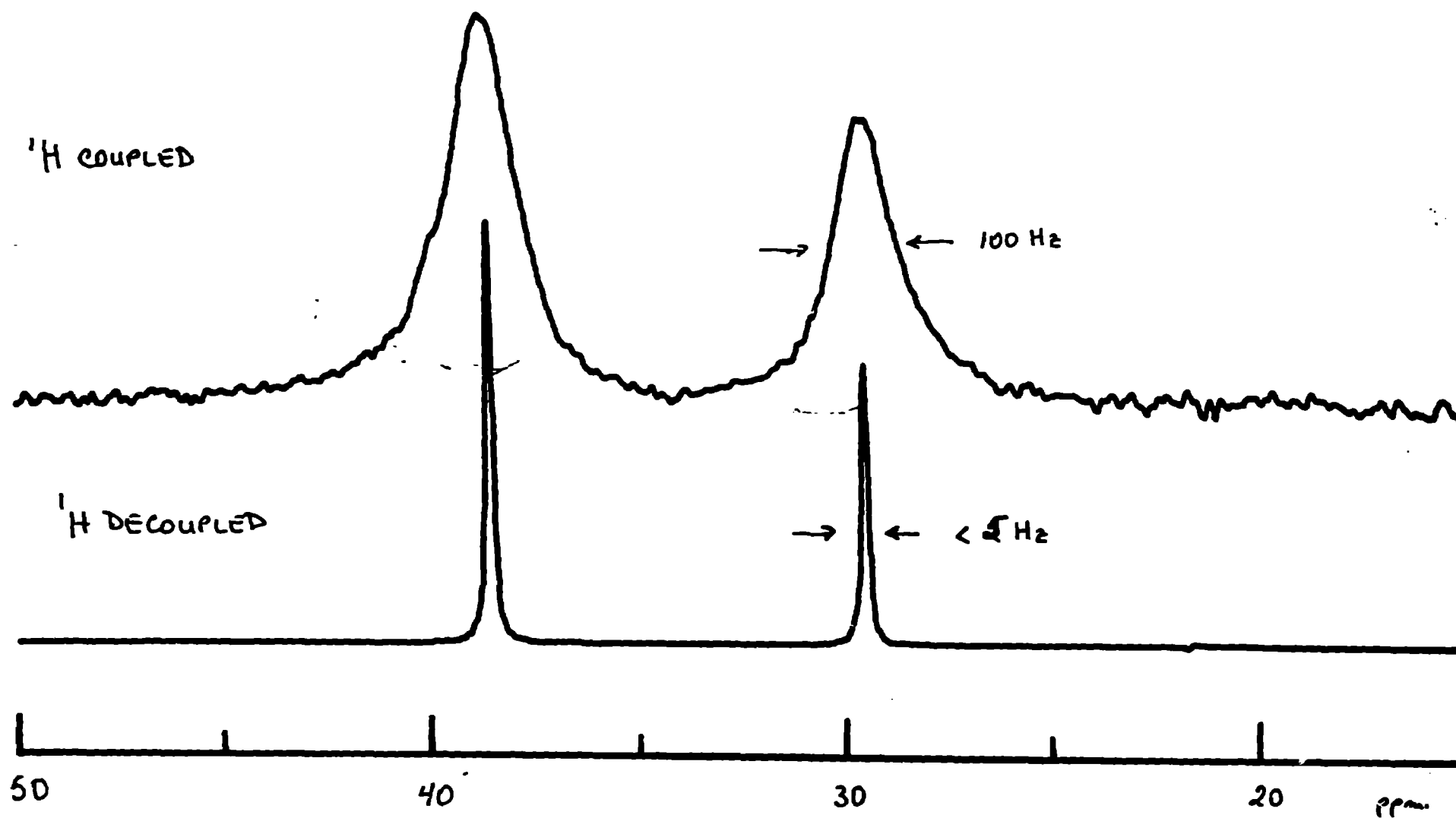
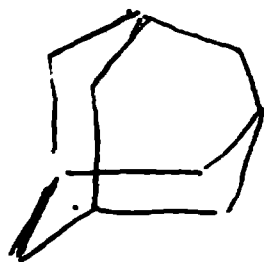
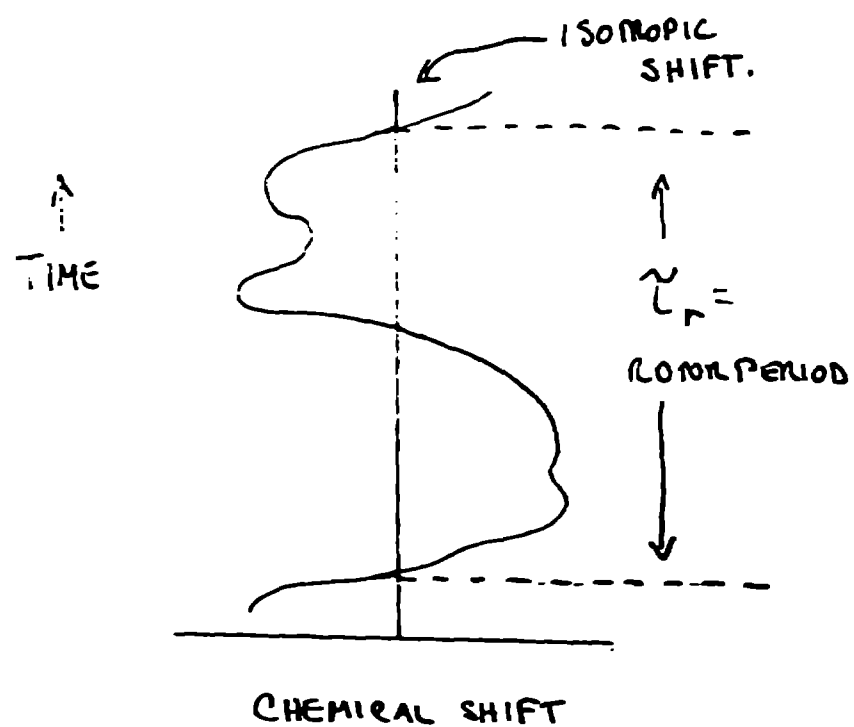


Figure 5

ADAMANTANE



TIME DEVELOPMENT OF
THE CHEMICAL SHIFT OF
A SPIW ISOCHROMAT.



FREE INDUCTION DECAYS

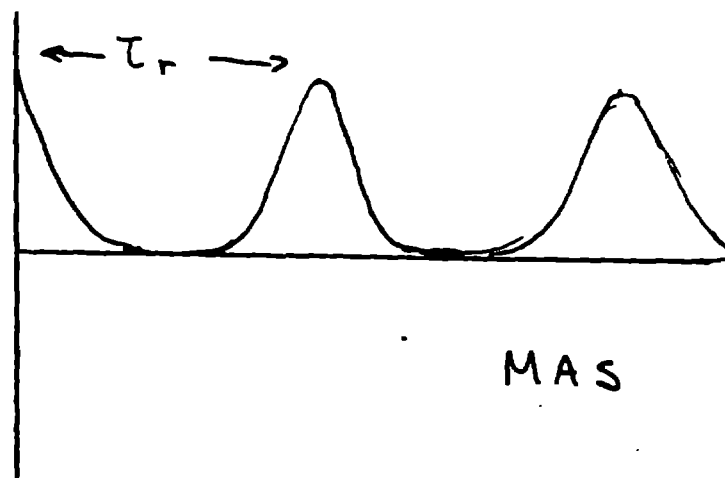
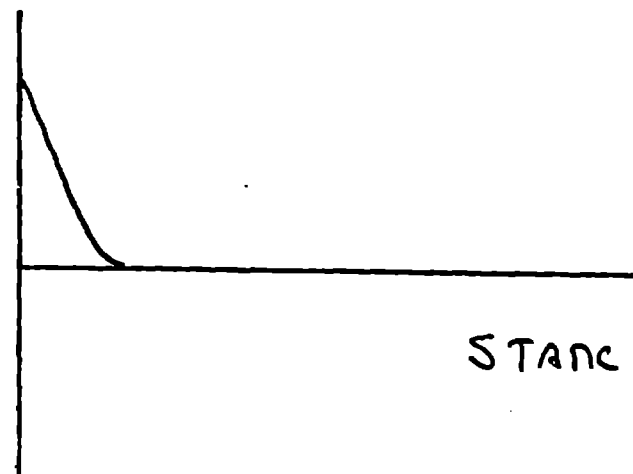


FIGURE 6

FIGURE 7

POLYETHYLENE
OXIDE

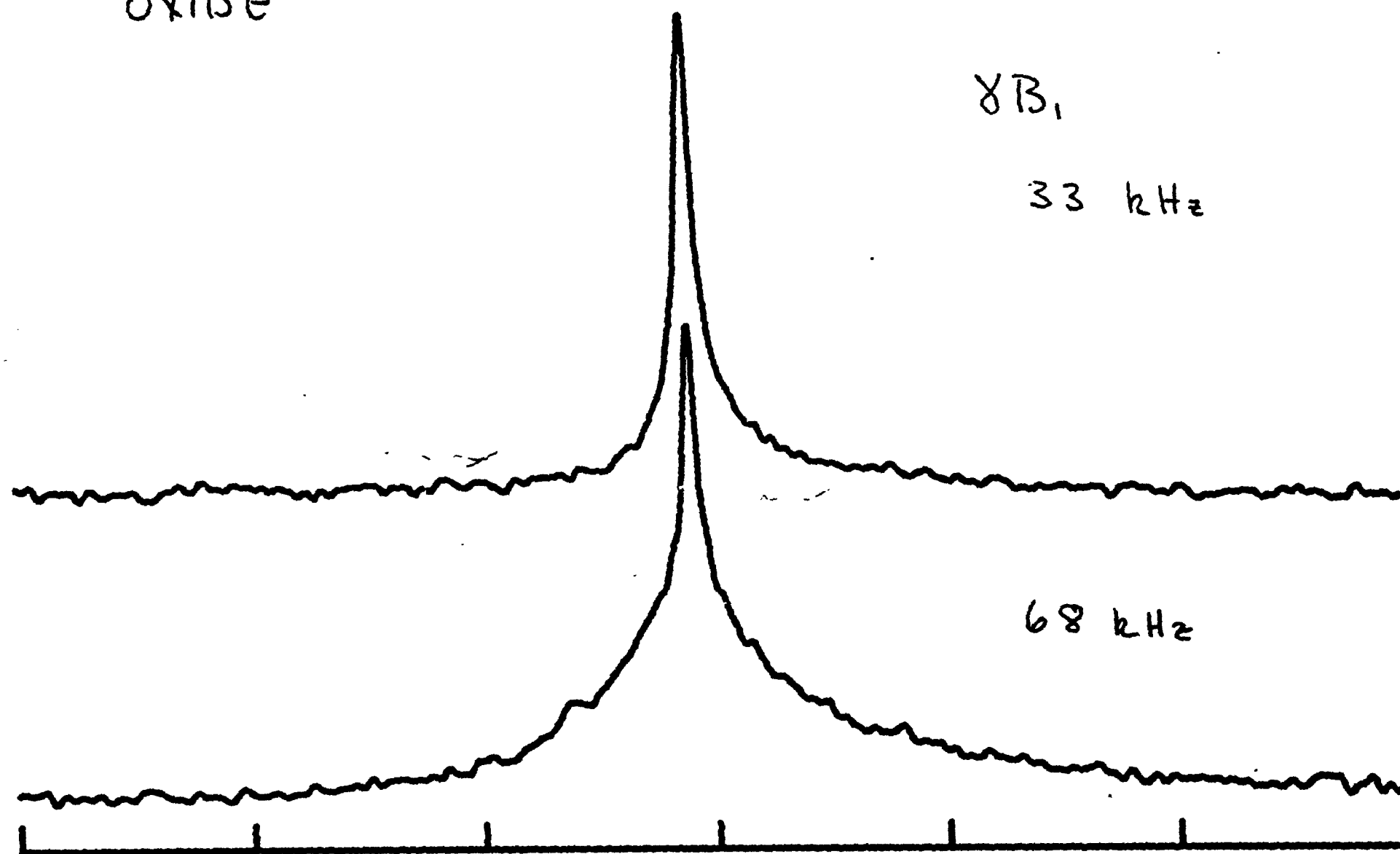


FIGURE 8

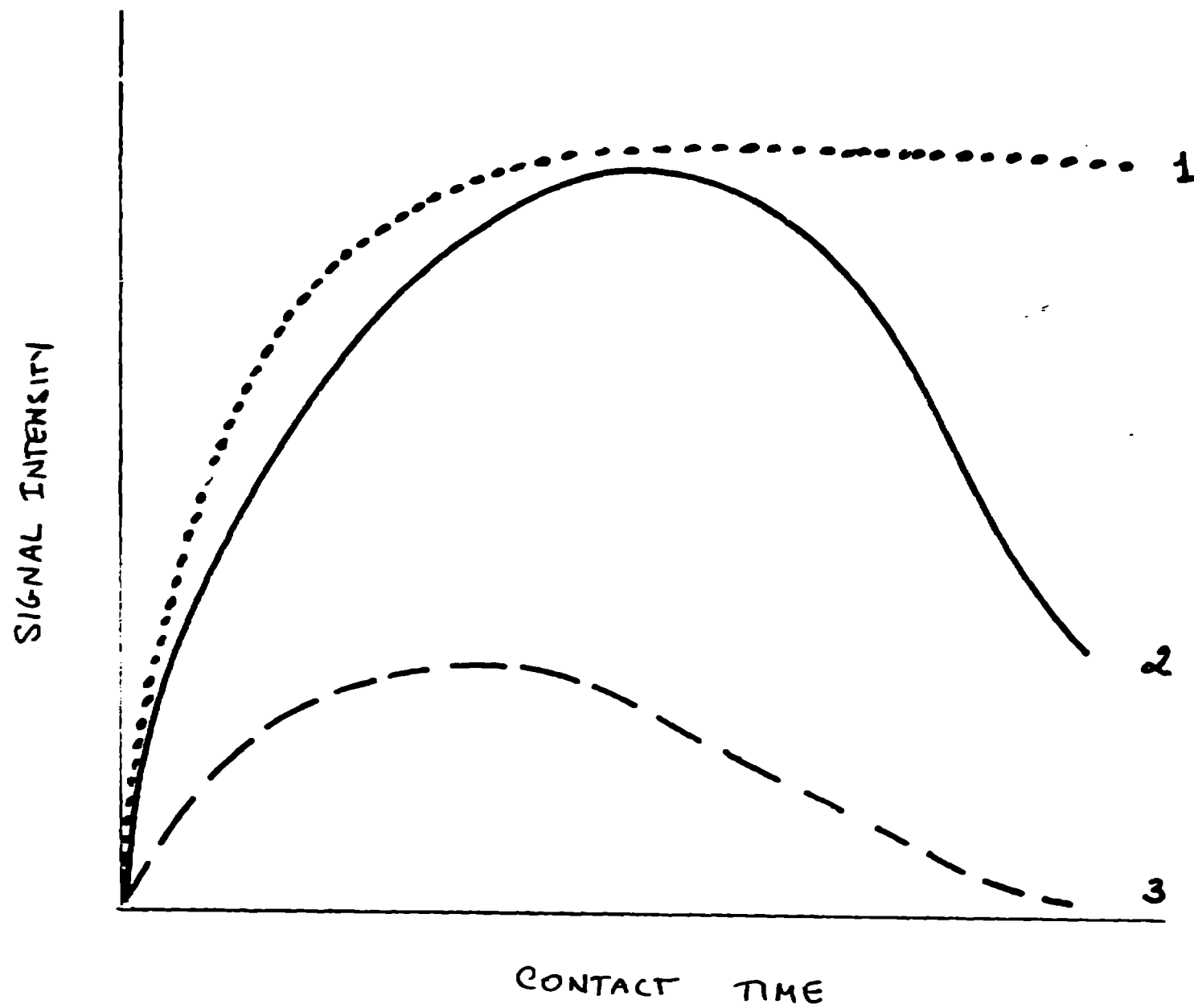


Figure 9

CORN SEEDS.

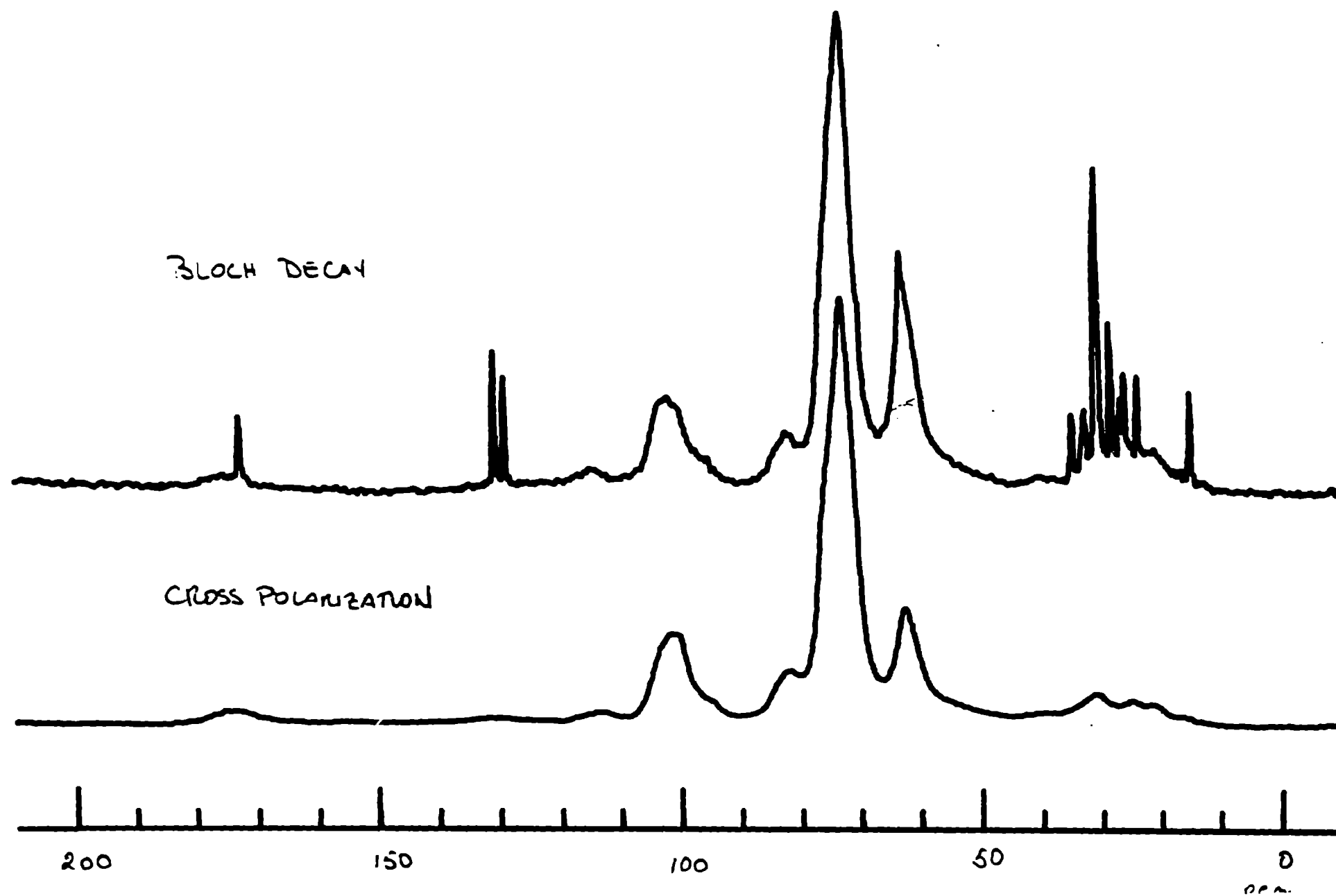


FIGURE 10

ARMADALE FULVIC ACID.

